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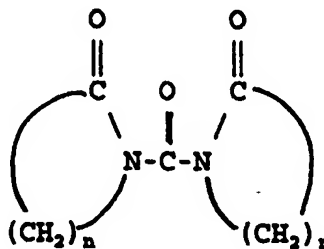
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(54) Title: HIGH-MOLECULAR POLYAMIDE

(57) Abstract

The invention relates to a process for preparing a high-molecular polyamide or polyester by melt-mixing polyamide or polyester having a lower molecular weight with a carbonyl bislactam having formula (1), in which n = an integer of between 3 and 15. With the process according to the invention a permanent increase in the molecular weight of a polyamide is obtained within 2 minutes, whereas this takes at least 10 minutes under comparable conditions using a bislactam according to the state of the art.



(1)

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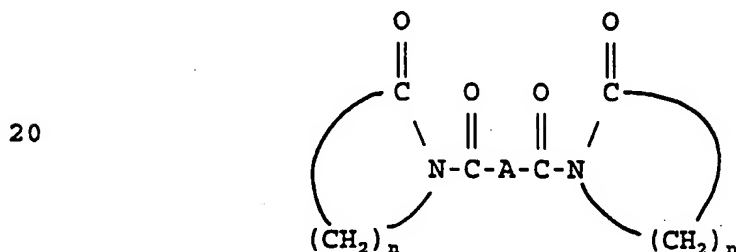
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HIGH-MOLECULAR POLYAMIDE

The invention relates to a process for preparing a high-molecular polyamide, polyester or polyester-amide block copolymer by melt-mixing
 10 polyamide or a polyester or a mixture of a polyamide and a polyester having a lower molecular weight with a bislactam.

Such a process is for example known from EP-A-0288253, in which, as in other publications, use
 15 is made of bis-N-acyl lactams having the formula:



25 in which A = alkyl or an aromatic group and n is generally between 3 and 11.

The bis-N-acyl lactams used in the examples are generally tere- or isophthaloyl bislaurocaprolactam or biscaprolactam.

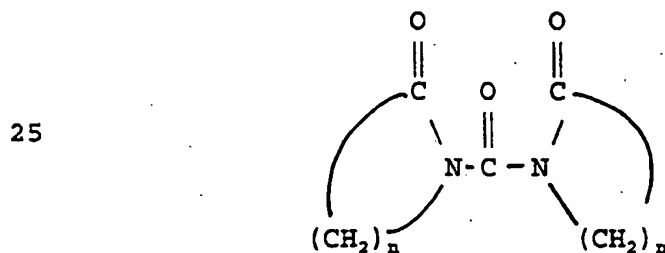
30 These bis-N-acyl lactams however have the drawback of a relatively low reaction rate, as a result of which long reaction times are required to realize the desired increase in molecular weight, which may lead to undesired side-reactions, e.g. discolouration
 35 of the polyamide or polyester.

In practice, bisoxazolines or bisoxazines are therefore more preferably used as chain extenders for polyamides. The drawback of these is however that they react with the polyamide's carboxylic end groups, as a result of which the polyamide obtained contains excess amino end groups and the polyester excess hydroxyl endgroups, which adversely affects the thermal oxidative stability.

The invention's aim is hence a process in which a bifunctional chain extender that does not involve the above drawbacks is added to a polyamide or a polyester melt.

The inventors have now most surprisingly found that when the polyamide or the polyester having the lower molecular weight reacts in the melt with a carbonyl bislactam, a colourless, stable polyamide or polyester with increased molecular weight is very quickly obtained.

'Carbonyl bislactam' is understood to be a compound having the formula:



30 in which n is an integer of between 3 and 15.
Preferably n = 5 to 12.

The carbonyl bislactam can be obtained in a simple manner through reaction of the lactam with

phosgene, COCl_2 . The preparation of N,N'-carbonyl biscaprolactam via this route in benzene in the presence of a tertiary alkylamine as a catalyst is for example described in JP-A-42017832.

5 The amount of carbonyl bislactam used in the process according to the invention may vary within a wide range. Usually at least about 0.1 wt.%, relative to the polyamide or the polyester, will be required to obtain an appreciable effect. Amounts of more than 4
10 wt.% do not usually lead to a further increase in the molecular weight.

 Usually a person skilled in the art will adjust the amount of carbonyl bislactam to be used to the number of amino or hydroxyl end groups available
15 and the increase in viscosity to be realized as a result of the increased molecular weight. He will usually determine the optimum amount for his situation through simple experimentation.

 In principle, the process of the invention
20 can be used for all types of polyamides and polyesters. The polyamides include at least the aliphatic polyamides, for example polyamide-4, polyamide-6, polyamide-8 etc., polyamide-4,6, polyamide-6,6, polyamide-6,10, etc., polyamides derived from an
25 aliphatic diamine and an aromatic dicarboxylic acid, for example polyamide-4,T, polyamide-6,T, polyamide-4,I, etc., in which T stands for terephthalate and I for isophthalate, copolyamides of linear polyamides and copolyamides of an aliphatic and a partially aromatic
30 polyamide, for example 6/6,T, 6/6,6/6,T, etc. The process is particularly advantageous in the case of

partially aromatic polyamides and copolyamides that require in general a relatively long polymerisation time.

The polyesters include at least polyesters
5 derived from aliphatic dicarboxylic acids and diols, polyesters from aliphatic diols and aromatic dicarboxylic acids, copolyesters that are partially aliphatic and partially aromatic and polyesters that contain units derived from cycloaliphatic dicarboxylic
10 acids. Specific examples are polybutylen adipaat, polyethylen terephtalate, polyethylen naphtalate, polybutyleenterephtalate, copolyesters of polybutylenadipate and polybutyleenterephtalate, the polyester derived from butanediol and cyclohexane
15 dicarboxylic acid.

The process according to the invention can be carried out in a simple manner using the usual melt-mixing techniques and equipment, for example by dry
blending the polyamide or polyester having a lower
20 molecular weight and the bislactam and optionally also other additives in a solid state, for example in a tumbler drier, after which the mixture obtained is melted in a usual melt-mixing apparatus, for example a Haake kneader, a Brabender mixer or a single- or
25 double-screw extruder. The different components can also be fed to the mixing apparatus separately.

Best results are obtained if the lower molecular polyamide or polyester are thoroughly dried.

Preferably the carbonyl bislactam is added
30 to the melted polyamide or polyester product stream in the polymerisation process as it leaves the

polymerisation reactor. The polymerisation process can be carried out both batchwise or in a continuous mode. In the first case a reduction of the residence time in the reactor can be realized and thus an increase in productivity; with the continuous process the after-condensation step, that is necessary usually to obtain a polyamide or polyester of sufficient molecular weight can be avoided.

The invention will now be elucidated with reference to the following examples; without however being limited thereto.

Materials used :

- a.1. polyamide-6 having a $\eta_{rel} = 2.56$ measured in formic acid and a concentration of end groups - COOH = 0.052 meq/g -NH₂ = 0.052 meq/g.
- a.2. polyethylene terephthalate, PET, having a $\eta_{rel} = 1.44$, measured in m-cresol
- b.1. carbonyl biscalpitolactam (CBC); from Isochem, France.
- b.2. N,N'-isophthaloyl biscalpitolactam (IBC): from DSM RIM NYLON, the Netherlands.
- c. 1,3 phenylene bisoxazoline (1.3 PBO): from Takeda Chemicals, Japan.

Process:

The polyamide was melted in a Brabender mixer, type Plasticorder 651, at 240° C until a constant torque of the kneaders was obtained, after which the bislactam was added and the mixing was continued. The kneaders'

torque was measured at different times. The mixing was carried out at a rotational speed of the kneaders of 30 rotations per minute, under a nitrogen blanket to prevent the risk of the polyamide decomposing as a result of oxidation.

Table 1 shows the compositions investigated and the results of the measurements.

The results of Experiments 2 vs. 4 show the surprisingly high activity of the carbonyl lactam, as a result of which a stable high value of the melt viscosity (expressed as the Brabender mixer's moment of couple) was obtained after 2 minutes already, whereas this is not the case when use is made of the bislactam according to the state of the art.

Thanks to this short reaction time, which is of the same order as the residence time in a normal extrusion, a stable, increased melt viscosity can be realized in practice, and the molecular weight of polyamide can be increased, using only a bislactam.

The relative viscosity, measured in a solution of 1 gram in 100 ml of 90 wt.% formic acid, shows the same development as the measured moments of couple after 10 minutes.

Table 1

Experiment	1	2	3	4	5	6
Composition (parts by weight)						
a.1.	100	100	100	100	100	100
b.1. *) CBC		0.666	0.666			
b.2. *) IBC				0.940		0.940
c. *) PBO			0.570		0.570	0.570
Kneader couple-moment (Nm)						
2 min.	6.0	9.5	10.5	7.0	6.0	8.4
4 min.	6.0	9.5	13.5	7.2	7.5	10.5
6 min.	6.0	9.5	16.5	8.5	8.5	11.5
10 min.	6.0	9.5	19.5	8.4	10.5	13.0
relative viscosity (10 min.) in formic acid	2.6	2.9	3.9	2.7	2.9	3.2

*) the quantity (b) resp. (c) was chosen equivalent to the number of amino resp. carboxyl endgroups available in the polyamide.

The process of the foregoing experiments was repeated however with polyethylene terephthalate having a solution viscosity of 1.44 in m-cresol. The temperature was set at 280 °C. Compositions and results
5 are given in Table 2.

Table 2

Experiment	7	8	9	10	11	12
Composition (parts by weight)						
a.2.	100	100	100	100	100	100
b.1. CBC **)				0.96		0.96
b.2. IBC **)			1.35		1.35	
c. PBO **)		0.27			0.27	0.27
Kneader couplemoment (Nm)						
2 min.	0.5	1.0	1.5	1.5	2.0	1.5
4 min.	0.5	1.0	2.0	2.0	2.5	2.0
6 min.	0.5	1.0	2.5	2.0	3.5	2.5
10 min.	0.5	1.0	2.5	2.5	4.5	2.5
relative viscosity (10 min.)	1.44	1.47	1.62	1.62	1.68	1.64
in m-cresol 1 wt.%, 135°C						

**) The quantity (b) resp. (c) was chosen equivalent to the number of hydroxyl resp. carboxyl end groups.

5 Analysis of the endgroups after 10 minutes meltmixing reveals for the compositions the following data:

Table 3

Experiment	COOH- [meq/gram]	OH- [meq/gram]
7	0.041	0.083
8	0.026	0.085
9	0.046	0.031
10	0.029	0.047
11	0.027	0.028
12	0.018	0.045

10

Apparently the carboxy biscalpitolactam (CBC) is also reactive with the carboxyl endgroups. IBC reacts with the hydroxyl end groups only, and seems to be more effective. However also IBC shows to be effective for 50% only. For this reason the added quantities IBC and CBC were increased in a further experiment by 50%. Very surprisingly in this case CBC showed much more effectivity than IBC.

15

Results are given in Table 4.

Table 4

5

Experiment	-COOH meq/gram	η_{rel}	remarks
7	0.041	1.44	
9 *)	0.045	1.63	
13	0.045	1.69	2.03 pbw IBC
10 *)	0.028	1.65	
14	0.021	1.77	1.44 pbw CBC

*) duplo experiments

Therefore CBC is used in polyesters
10 preferably in excess of the equivalent quantity
calculated on the basis of hydroxyl endgroups available
in the lower molecular polyester of which the molecular
weight should be increased.

The molecular weight of the polyamide or
15 polyester having the lower molecular weight may vary
over a wide range and is mainly determined by
economical reasons and the source of the material. In
general it may vary from about 1000 to about 20.000
expressed as number averaged molecular weight M_n .
20 However situations are possible in which a mixture
containing a polyamide or polyester of high molecular
weight for instance 25.000 and an appreciable fraction
oligomeric polyamide or polyester of molecular weight

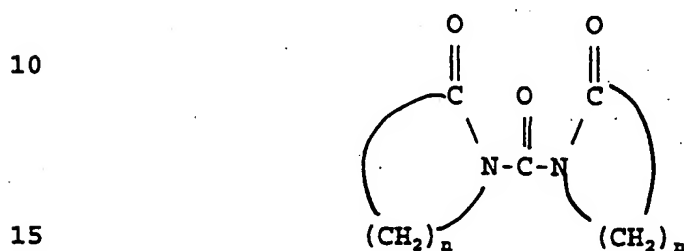
less than 1000 is reacted in the melt with the CBC according to the present invention.

The molecular weight of the high molecular weight polyamide or polyester to be produced by the process of the invention can be freely chosen and generally is higher than 15.000, preferably higher than 20.000, even more preferably higher than 25.000.

The polyamide or polyester obtained by the process of the invention can be processed by injection moulding, extrusion or blow moulding to obtain moulded articles, and by melt spinning to obtain fibres.

C L A I M S

1. Process for preparing a high-molecular polyamide
or polyester by melt-mixing a polyamide or
5 polyester having a lower molecular weight with a
bislactam, characterised in that the bislactam is
a carbonyl bislactam having the formula:

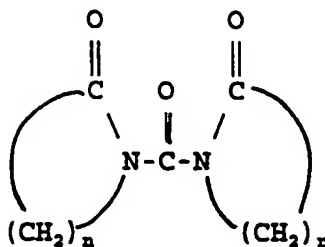


- in which n = an integer of between 3 and 15.
2. Process according to Claim 1, characterised in
that n = 5 to 12.
- 20 3. Process according to Claim 1 or Claim 2,
characterised in that use is made of 0.1 to 4 wt.%
of the bislactam, relative to the polyamide or the
polyester.

FORMULA SHEET

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10



15

formula 1

INTERNATIONAL SEARCH REPORT

national Application No
PCT/NL 98/00217

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G69/48 C08G69/18 C08G69/20 C08G63/91

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 288 253 A (POLYPLASTICS CO) 26 October 1988 cited in the application see claims 1-4, 6-8 ---	1-3
A	EP 0 117 433 A (GOODRICH CO B F) 5 September 1984 see claims 1-10 ---	1-3
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 494 (C-651), 8 November 1989 & JP 01 197526 A (TEIJIN LTD), 9 August 1989, cited in the application see abstract --- -/--	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 533 650 A (MONSANTO CO) 29 November 1978 see claims 1,2,4 see page 1, column 2, line 80 - line 88 ---	1-3
A	WO 96 34909 A (DSM NV ;LOONTJENS JACOBUS ANTONIUS (NL); DERKS FRANCISCUS JOHANNES) 7 November 1996 see claims 1,2,6 ---	1-3
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 569 (C-666), 15 December 1989 & JP 01 236238 A (TEIJIN LTD), 21 September 1989, see abstract -----	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

PCT/NL 98/00217

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0288253 A	26-10-1988	JP 1861009 C JP 63265964 A	27-07-1994 02-11-1988
EP 0117433 A	05-09-1984	CA 1214012 A JP 59138226 A	18-11-1986 08-08-1984
GB 1533650 A	29-11-1978	BE 849770 A DE 2657935 A FR 2352013 A FR 2361431 A JP 52078997 A NL 7614132 A SE 7614381 A	22-06-1977 23-06-1977 16-12-1977 10-03-1978 02-07-1977 24-06-1977 23-06-1977
WO 9634909 A	07-11-1996	BE 1009365 A AU 5409196 A EP 0835276 A	04-02-1997 21-11-1996 15-04-1998